

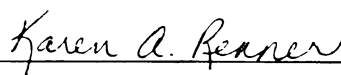
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**FACTORS INFLUENCING SUGAR BEET RESPONSE
TO NICOSULFURON AND PRIMISULFURON**

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KAREN M. NOVOSEL

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**FACTORS INFLUENCING SUGAR BEET RESPONSE
TO NICOSULFURON AND PRIMISULFURON**

By

Karen M. Novosel

A THESIS

**Submitted to
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ABSTRACT

FACTORS INFLUENCING SUGAR BEET RESPONSE TO
NICOSULFURON AND PRIMISULFURON

By
Karen M. Novosel

Nicosulfuron and primisulfuron are two sulfonylurea herbicides that may persist in the soil and injure sugarbeet. Sugarbeet response was measured one and two years after herbicide application at five sites. Nicosulfuron did not injure sugarbeet at any site. Sugarbeet yield was reduced one year following application of primisulfuron. IG_{50} values for primisulfuron were consistently lower than those of nicosulfuron. Sugarbeet response was highly correlated to % organic matter ($R^2 = .88$). K_d values for nicosulfuron were lower than those of primisulfuron. In hydroponics, primisulfuron had an IG_{50} value of 1.9 ppb while nicosulfuron had an IG_{50} value of 8.9 ppb, regardless of solution pH. Uptake of primisulfuron was three times that of nicosulfuron. Nicosulfuron translocation was more rapid, but there was no difference in the total amount of herbicide translocated. Increased susceptibility of sugarbeet to primisulfuron was due to increased sensitivity.

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Chapter 1

LITERATURE REVIEW

Sulfonylureas are a herbicide family applied for preemergence and postemergence weed control in many agricultural systems. This group of chemicals is characterized by low use rates and low mammalian toxicity (4,12,16). Typical visual injury symptoms include interveinal chlorosis or purpling of grasses, and similar discoloration as well as stunting of broadleaf species. Soil factors influencing sulfonylurea degradation, persistence and bioavailability are important because of the impact these compounds have on the environment and sensitive rotational crops such as sugar beets. The following review examines the history of this class of herbicides, their soil interactions, the effect of sulfonylurea soil residues on sensitive rotation crops, and uptake, translocation, metabolism, and ALS sensitivity of sulfonylureas.

History and General Structure. The discovery of the herbicidal properties of the sulfonylureas occurred in 1966 in Germany. The first compounds were derivatives of another class of herbicides, the triazines (4). The DuPont corporation patented the earliest sulfonylurea herbicide in 1977 (5,11), and it was five years before any other company patented a pesticide in this class. Chlorsulfuron, marketed under the trade name

Glean, was the first commercially available sulfonylurea, and is still sold for weed control in a variety of cereal crops. Since the discovery of this herbicide class, over fourteen different companies have obtained sulfonylurea patents, spanning hundreds of compounds.

Despite the wide variety of sulfonylureas, a basic structure is common to the family. This common framework consists of: an aryl portion, the sulfonylurea bridge, and a nitrogen containing heterocycle (5,35). Breakdown in the soil by chemical means usually occurs through hydrolysis of the bridge portion of the molecule (12,33,47). Microbial degradation pathways include bridge cleavage, methyl group hydroxylation, demethylation followed by hydroxylation, and deesterification resulting in free acid formation (5). Metabolism in plants occurs predominantly by aryl hydroxylation followed by glucose conjugation (12,29,35).

The literature on sulfonylurea herbicides is extensive. This review will focus on the sorption, degradation, and persistence of sulfonylureas in soil, the response of rotational crops to sulfonylureas, and uptake, translocation and metabolism of sulfonylureas in plants.

Sorption. The pH dependent ionization of the sulfonylurea herbicides directly affects the sorptive properties of these compounds. Chlorsulfuron has been the most thoroughly studied member of this family because it was the first registered

compound in its class. Acidic conditions in the soil reduce the water solubility of chlorsulfuron and could reduce the mobility of the compound in the soil (41).

In a study performed by Wehtje et al.(65), the pH influence on sorption of sulfmeturon was demonstrated. Sorption of the anionic species of sulfmeturon was dependent on the iron and aluminum oxide content in weathered soils, such as those found in the American southeast. The surface charge of these soil minerals is pH dependent and is neutral in a pH range of 6.0 to 8.5. Below 6.0, the charge is positive due to a proton accumulation at the soil colloid surface. Above the PZNC (Point of Zero Net Charge), OH⁻ buildup imparts a negative charge to the particles. In this study, as in others, as the soil pH increased and the herbicide became more negatively charged, the herbicide sorption decreased. This resulted in an increase in availability and an increase in plant uptake (2,3,42). Increased uptake could lead to increased herbicide efficacy but also increases the potential for injury to sensitive crops.

One of the most important factors in the sorption of any herbicide is the organic matter content of the soil. The exact mechanisms involved in sorption can only be postulated because of the heterogeneous, amorphous nature of both the humic and non-humic portions of the organic matter polymer (58). The ability of organic matter to interact with organic compounds, such as herbicides, stems from the oxygen containing

functional groups found in the humic components (58). Typical bonding mechanisms for the adsorption of the sulfonylureas to organic matter are: Van der Waals forces, hydrogen bonding, and ligand exchange (58). The ionization of the functional groups on the organic matter moiety depends on the pH of the soil water with an acidic pH protonating many of the functional groups resulting in a predominantly neutral molecule. Past findings have indicated that herbicide sorption may result from partitioning of the herbicide into hydrophobic micelles (58). However, these claims have never been confirmed, and evidence (41,42,61) suggests that there are sorption sites where the herbicides bind. Until the structure of organic matter and its various components is discerned the pathways are conjectural.

Another experiment examining sulfonylurea sorption to various soil components was performed by Borggaard and Streibig in Denmark (10). They investigated chlorsulfuron sorption to humic acid, a variety of iron oxides, and a montmorillonite clay by simulating field conditions at a pH range of 4.0 to 8.0. The results were analogous to Stevenson's (58), i.e., that iron oxides adsorbed chlorsulfuron over the pH range of 4.0 to 8.0 and montmorillonite did not adsorb chlorsulfuron at any pH. Humic acid adsorbed chlorsulfuron below pH 8.0 and goethite (an iron oxide) adsorbed below pH 6.0 (10). Stevenson postulated that montmorillonite did not sorb or affect herbicide mobility because the herbicide could

not enter the inner sites of the clay matrix causing a sieving effect (58).

Degradation

Hydrolysis. Sulfonylureas are weakly acidic compounds having a pKa range of 3.3 to 5.4. The pKa values of nicosulfuron and primisulfuron are 4.3 and 4.5, respectively. These compounds also have an alkaline pKa value which exceeds pH 10. Bulk soil pH has a major effect on water solubility, K_{ow} , and the chemical reactions these compounds undergo in the soil (5,6,12). The most common reaction occurring in soil is a hydrolysis reaction with the general form outlined in Figure 1. This reaction takes place at an increased rate as the soil pH decreases because more of the herbicide is in the neutral form. Under extremely alkaline conditions such as pH > 10, a second ionization of the herbicides occur which also results in increased hydrolysis (5,12,29). Controlling the process of hydrolysis is the ionization of the sulfonylurea bridge. The neutral molecule is lipophilic and is therefore 250 - 1000 times more likely to hydrolyze (12). Microbial degradation occurs simultaneously through various mechanisms (4,31,39), but the primary degradation pathway in soil is chemical.

Research performed by Bergstrom in Sweden (2,3) suggested that though chlorsulfuron and metsulfuron-methyl are mobile in the soil, the rate of degradation limits movement of the herbicides. Neither herbicides moved below the top 10 cm of soil when applied at twice the normal use rate. Seven months

after application, less than 1% of either chemical applied at twice the standard rate could be detected (2,3).

Soil moisture content and temperature also influenced the rate of degradation in the soil (12,30). Fuesler and Hanafey (30) concluded that degradation increased on air dry soil as a function of temperature due to an increase in chemical hydrolysis. The breakdown pathway of chlorimuron they proposed is shown in Figure 1. The degradation products suggested that both microbial and chemical breakdown occurred in moist soils, while only hydrolytic degradation occurred in air dry soil. A reduction in the hydrolysis rate resulted from an increase in soil pH, which decreased overall degradation (66), and, therefore, increased soil persistence.

Persistence. Sulfonylurea persist in the soil long enough to injure sensitive rotational crops such as sugar beets (52). Tolerance to residual amounts of a herbicide is dependent on the species of plant, the particular herbicide, and the amount of chemical the plant intercepts. Problems that can occur as a result from a long soil residual include rotation crop injury and decreased crop yield. Rotation restrictions are sometimes inadequate and labels are modified if persistence problems arise.

Chlorsulfuron and metsulfuron-methyl were sold as a formulated mixture in the United Kingdom but was removed from the market because of the long soil persistence of

chlorsulfuron. In response to this problem, a computer model was developed to predict sulfonylurea movement and persistence in the soil. Timing of application, spring vs. autumn, greatly affected the accuracy of the model (6), as did the prediction of herbicide fate under wet soil conditions. The program tended to overestimate movement through the soil profile and, therefore, underestimated the amount of herbicide the root intercepted (6).

Brewster and Appleby (11) compared various rotation crop responses to chlorsulfuron. A reduction in sugar beet foliage dry weight occurred for 26 months after application. Yields of Italian ryegrass, oilseed rape, and alfalfa were reduced up to 9 months after application. Snap bean and sweet corn were only injured for 5 months following application, while wheat exhibited no deleterious effects in that same time period. Rahman (50) reported no detectable primisulfuron in a sandy loam soil at pH 5.7 sampled 120 days after treatment using a mustard bioassay.

Repeated applications of chlorsulfuron did not lead to increased persistence even when applied four times at twice the normal use rate (66). The experiment was conducted under dryland conditions, with a soil pH of 6.5 to 8.1. Not only was there a lack of cumulative effect from repeated applications, but there was no acceleration in breakdown (66). This data led researchers to conclude that chemical hydrolysis is the primary degradation pathway in dry soils although there are

primary degradation pathway in dry soils although there are herbicides whose primary degradation pathway is microbial that do not exhibit accelerated breakdown in the presence of more herbicide. The persistence of chlorsulfuron was attributed to the high pH more than the lack of rainfall.

Movement and Metabolism. Primisulfuron is absorbed primarily through plant foliage but also possesses some soil activity (50). After foliar uptake, the herbicide is translocated in the phloem to the meristematic regions of the plant. Cessation of cell division occurs immediately but total plant desiccation takes approximately 10 to 20 days. Death occurs due to an interruption in the synthesis of the branch chain amino acids valine, leucine, and isoleucine (3,4,5).

Sulfonylureas inhibit the acetolactase synthase enzyme (ALS). This enzyme catalyses the initial reactions in the synthesis pathways of the branch chain amino acids (5,12,32). In the formation of valine and leucine, two molecules of pyruvate are condensed to form alpha-acetolactate + CO₂ (55). In the synthesis of isoleucine, the initial reaction is a condensation reaction between one molecule of pyruvate and one molecule of 1 alpha- ketobutyrate resulting in alpha-aceto-alpha-hydroxybutyrate + CO₂ (55). The interference of amino acid synthesis results in a lengthy time period before injury symptoms appear (15,24).

ALS Sensitivity, Uptake/Translocation and Metabolism. There are three proposed mechanisms for observed differences in plant species tolerance to sulfonylurea. These include 1) a difference in ALS sensitivity between tolerant and susceptible species, 2) a difference in plant uptake and /or translocation, and 3) differential metabolism.

Herbicides such as the aryloxyphenoxypropionates and the cyclohexadiones show a difference in enzyme sensitivity as the main factor influencing species response (12). However, ALS enzyme isolated in tolerant and susceptible species of plants had a limited range of sensitivity to any given sulfonylurea (5). This indicated that differential enzyme sensitivity was not the factor conferring tolerance. Research conducted on ten corn genotypes expressing variable sensitivity to thifensulfuron indicated that differences in response were a result of relative efficiencies in metabolism and not in any dissimilarity of the enzyme (25). Further evidence to support this proposal was presented by Moberg (43). He concluded that all cases of naturally occurring crop selectivity are not due to ALS sensitivity but rather due to differences in metabolic detoxification (43).

ALS sensitivity, however, has been reported to be the cause of differential tolerance in genetically engineered plants as well as in weed species that developed resistance (16,34,44). Genetically engineered sugar beets tolerance to primisulfuron and thifensulfuron was due to altered ALS enzyme

sensitivity (34). The ALS enzyme isolated from resistant varieties of chickweed (Stellaria media(L.)) was insensitive to chlorsulfuron with respect to the normal biotype (16). Some cross resistance was noted but this alteration in enzyme sensitivity did not confer cross resistance to all sulfonylureas and imidazolinones (16).

Small variations in uptake, expressed as a percent of control, could not account for differences in barnyardgrass (Echinochloa crus-galli) response to primisulfuron (14,28,60). The tolerant variety translocated more herbicide than the sensitive biotype. This excluded the possibility that reduced uptake and/or translocation was the mechanism of tolerance.

Sweester, Schow, and Hutchinson were the first to report the mechanism of differential tolerance as metabolic deactivation (60). Specifically, they characterized the metabolites of chlorsulfuron through the use of mass spectroscopy, nuclear magnetic resonance spectroscopy, and high performance liquid chromatography and found a dramatic increase in the formation rate of the metabolic products in tolerant grass species (60). No differences were found in the rate of uptake and translocation but there was a high correlation with the rate of metabolism and plant tolerance. The metabolites that were formed were identified as the 5-OH derivative of chlorsulfuron and the 5-glycoside conjugate of chlorsulfuron (60). It was also noted that the conversion of the hydroxylated moiety to the glucose conjugated entity was

a very rapid process.

Hydroxylation followed by glucose conjugation is also the detoxification mechanism of primisulfuron. In barnyardgrass, the conversion takes place on the pyrimidinyl ring as opposed to the phenyl ring (44). Tolerance in broadleaf species is attributed to rapid inactivation by the same mechanisms but the reactions take place on either the phenyl or the heterocyclic ring non-preferentially (28) with a minor pathway being hydrolytic bridge cleavage. Removal of NADPH or O_2 caused a cessation of hydroxylation indicating the presence of a mixed function oxidase in the early stages of the metabolic pathway. The actual positions of the hydroxylations have not yet been determined but it is known that a cytochrome P-450 monooxygenase acts as the catalyst for this reaction (28).

Chlorimuron ethyl detoxification in soybeans (Figure 2) is due to a displacement of the pyrimidinyl chlorine by homoglutathione that has been conjugated with a sulfhydryl group (14). This was proven to be the major metabolite in broadleaf species with a minor metabolite being the deesterified molecule, chlorimuron. Increased broadleaf tolerance was due to increased metabolism (14).

Thifensulfuron methyl has the most metabolic pathways of all the sulfonylurea characterized to date (Figure 3). Thifensulfuron methyl is rapidly metabolized in soybean into a herbicidally inactive deesterified acid, thifensulfuron (14). There was no correlation between foliar uptake (as a

percent of applied) and species sensitivity which further discounted the possibility of uptake being the basis of tolerance. Sulfonylurea uptake and translocation depends on an acid trapping mechanism (14) and research (12,29,60) indicates that this cannot be solely responsible for differences in plant response.

Hydroponics. The technique for growing plants in the absence of soil is known as hydroponics. This type of growth system is utilized in the commercial production of vegetable crops such as lettuce, tomatoes, and cucumbers. Hydroponics can also be a useful scientific procedure, providing more uniform plant growth for use in experimentation. The literature on hydroponics in the determination of herbicide-plant interactions is limited (15,20,54), although it is a viable tool for the investigation of metabolism and the role that soil factors play in plant response to herbicides.

Atrazine uptake in oats decreased over time due to atrazines interference with carbohydrate production in the root (54). This reduced carbohydrate concentration in the root caused root necrosis. No information was found on plant response to sulfonylurea herbicides utilizing hydroponic experimentation.

Summary. A plethora of papers are available on the sulfonylurea herbicides, particularly chlorsulfuron. Soil pH greatly affects the behavior of these compounds. As the pH

increases, the rate of chemical hydrolysis decreases and thus persistence increases. Adsorption to soil decreases as the soil pH increases. Organic matter content increases sorption and persistence due to herbicide binding to various functional groups. Clay content has little effect on sulfonylurea sorption. Since all plants contain an ALS pathway, potential for plant injury exists but is species dependent. Tolerance is a result of differential metabolism of the herbicides with susceptible species metabolizing the compounds at a much slower rate.

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Figure 1. Generalized hydrolysis reactions of the sulfonylurea class of herbicides.

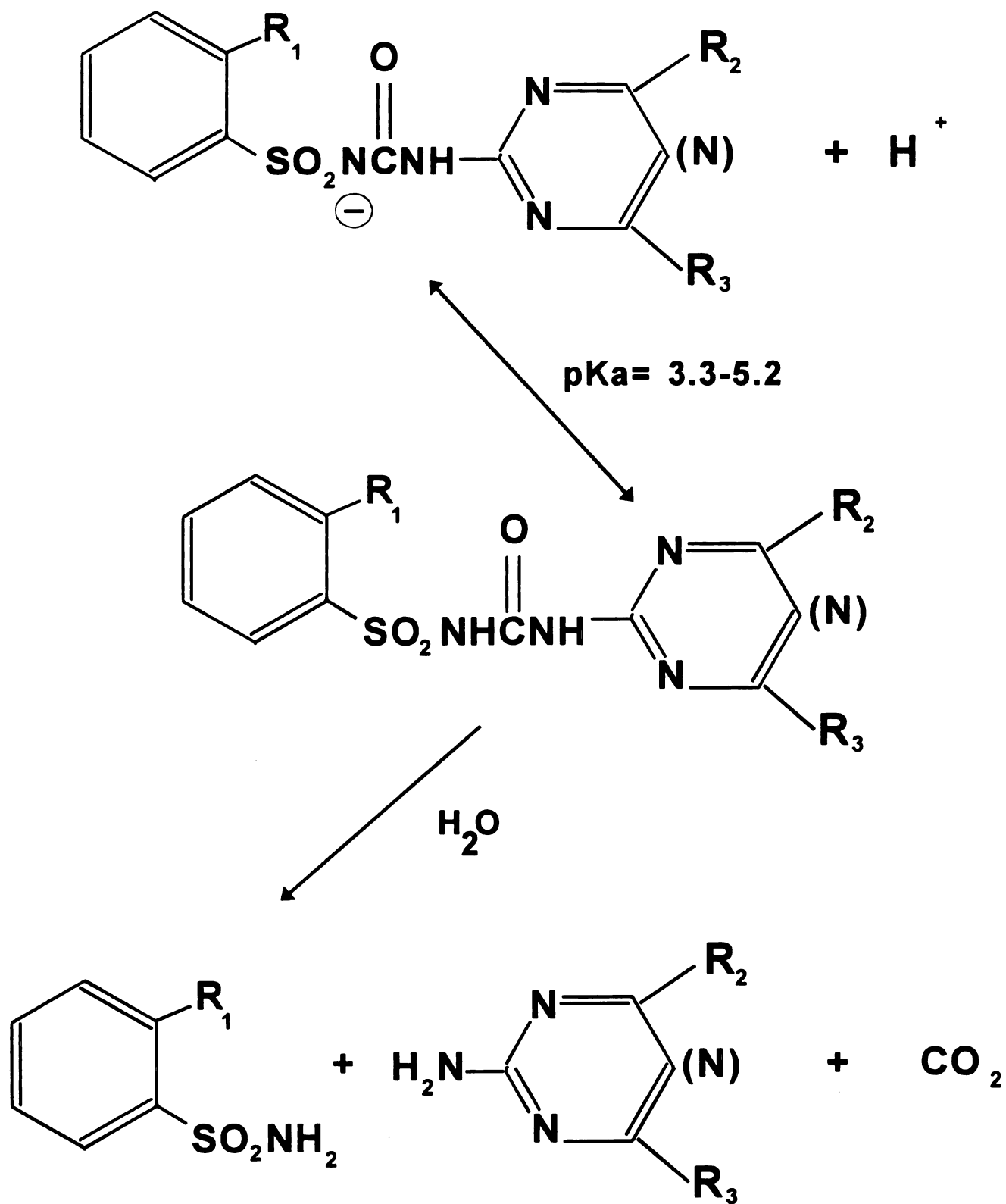


Figure 2. Chlorimuron ethyl detoxification reactions
in soybeans.

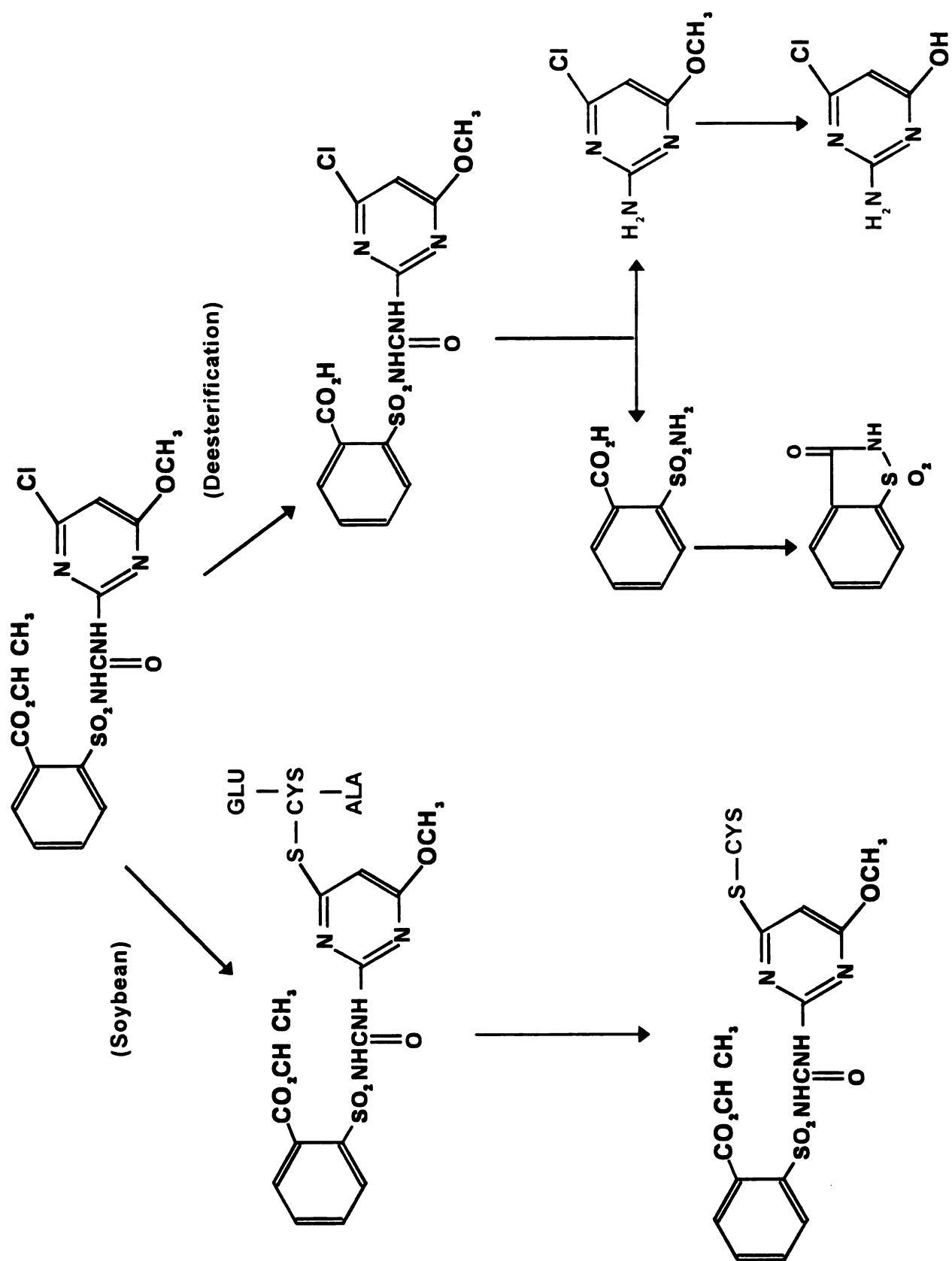
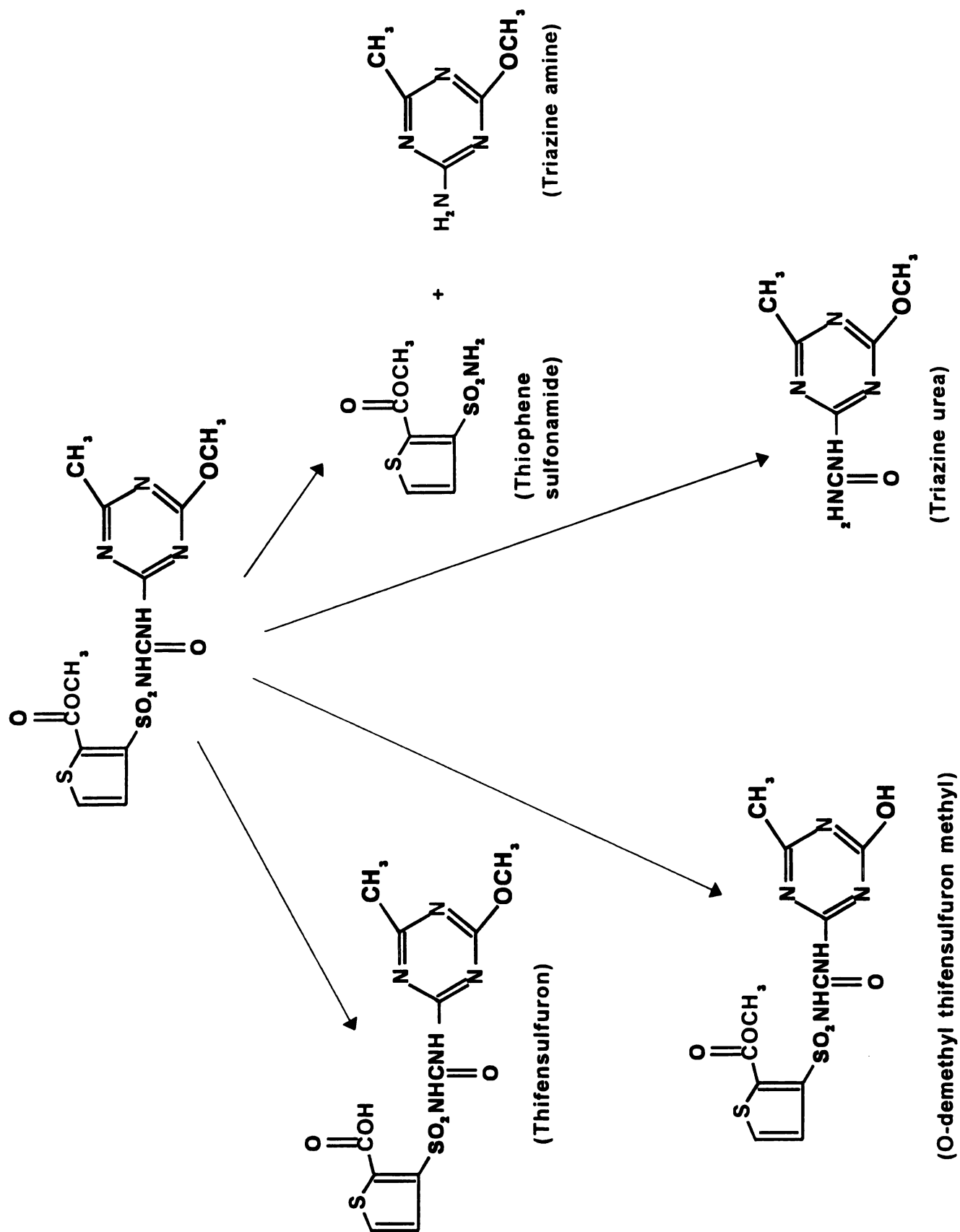


Figure 3. Metabolic deactivation pathways of thifensulfuron methyl.



Chapter 2

Influence of Soil on Sugar beet Response to Nicosulfuron and Primisulfuron

ABSTRACT

Nicosulfuron and primisulfuron are two sulfonylurea herbicides that have been observed to persist in the soil and injure sensitive rotational crops such as sugar beet (Beta vulgaris L.). Field and greenhouse studies were conducted to determine sugar beet response to these two compounds. Studies were initiated at four field sites to measure sugar beet response one and two years after nicosulfuron and primisulfuron application. Nicosulfuron at 70 and 140 g/ha and primisulfuron at 40 and 80 g/ha were applied postemergence to corn (Zea mays L.). At a fifth field site, 35 g/ha of nicosulfuron was applied to corn and sugar beet response observed one and two years after application. Nicosulfuron did not injure sugar beet at any site one or two years after application. In contrast, sugar beet yield was reduced one year after application of 40 and 80 g/ha of primisulfuron at both of the Saginaw sites. Visual injury was observed two years after application of 80 g/ha primisulfuron but this was not reflected in a yield reduction. Greenhouse studies determined sugar beet IG_{50} (inhibit growth by 50%) values for nicosulfuron and primisulfuron on four field soils, a muck, and a sand. IG_{50} values for primisulfuron were three times

lower than those of nicosulfuron for four soils indicating greater potential for sugar beet injury from primisulfuron. Sugar beet response was highly correlated to organic matter content ($R^2 = .88$) and not correlated to soil pH (pH range: 6.4-7.9). K_d values for nicosulfuron were lower than K_d values for primisulfuron for four of five soils indicating stronger affinity of primisulfuron for soil sorptive sites. K_d values for mineral soils were between .299 and .866 indicating a low sorptivity of both herbicides. **Nomenclature:** nicosulfuron, 2-[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]-N,N-dimethyl-3-pyridinecarboxamine; primisulfuron, 2-[[[(4,6-bis (difluoromethoxy)-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl] benzoic acid.

INTRODUCTION

Nicosulfuron and primisulfuron are two members of the sulfonylurea herbicide family. These compounds applied postemergence control perennial grasses such as johnsongrass (*Sorghum halapense* L.), quackgrass (*Elytrigia repens* L.) and some annual grasses and broadleaf weeds in field corn (*Zea mays* L.) (7,9). The sulfonylureas inhibit branched chain amino acid synthesis by interfering with the enzyme acetolactate synthase, commonly called ALS or acetohydroxyacid synthase (AHAS) (2,10).

Although these herbicides are degraded rapidly in soil,

residual amounts can persist and injure sensitive crops such as sugar beet. According to herbicide labels, sugar beets can be safely planted 10 months after nicosulfuron application if soil pH is less than 6.5 and after 18 months if soil pH exceeds 6.5 (7). Sugar beets may be planted 18 months after primisulfuron application regardless of soil pH (9). This may preclude the inclusion of sugar beet into a rotation the year following corn, but, more importantly, these herbicide labels are based on limited field studies. Soil factors, including soil pH, may play a role in the persistence and bioavailability of these two herbicides (11,12). As the pH increases, sorption to soil components decreases (3). The rate of chemical hydrolysis is therefore decreased and thus persistence increases (1). An understanding of soil-herbicide interactions and the role individual soil factors have on sorption, persistence, and bioavailability of these compounds is critical to predicting herbicide carryover and recommendations in sugar beet production areas.

Experiments were initiated to determine the response of sugar beet to nicosulfuron and primisulfuron at field sites and in the greenhouse. Soil sorption and desorption isotherms were constructed to determine if a difference in the sorptive properties of nicosulfuron and primisulfuron is a factor in sugar beet response.

MATERIALS AND METHODS

Field Studies. Characteristics of field site soils are given in Table 1.

Freeland sites. Nicosulfuron at 70 and 140 g/ha and primisulfuron at 40 and 80 g/ha were applied in a postemergence broadcast treatment in 1990 (site 1) and 1991 (site 2) to 13-25 cm corn. Plot size was 3 m by 10 m and applications were made with a tractor mounted compressed air sprayer in 206 L/ha of water at 208 kPa. In the year following herbicide application, dry beans, sugar beets, and alfalfa were planted in a randomized complete block design to determine rotational crop response. Field maintenance in 1991 included spring moldboard plow followed by a cultipacker. In 1992 the field site was fall chisel plowed and followed by a spring culti-mulch, field cultivation with a Triple K¹ at 8 cm depth, and was cultipacked. Visual injury was rated 60 days after planting (with 0 indicating no injury and 100% representing total plant death) and sugar beet stand counted 44 days after planting at both sites. Sugar beets were not harvested due to significant variations within replications as a result of soil pH.

Saginaw sites. Studies were conducted at two sites at the Saginaw Valley research facility. The first experiment was initiated in 1990 and the second in 1991. Nicosulfuron was

¹ Made by Kong Skilde. Kong Skilde Corporation, Bowling Green, OH 43402.

applied broadcast (POST) at 70 and 140 g/ha and primisulfuron was applied broadcast (POST) at 40 and 80 g/ha using a tractor mounted compressed air sprayer in 206 L/ha of water at 208 kPa to 28-35 cm corn. The year after herbicide application, dry beans, sugar beet, and alfalfa were planted in a randomized complete block design with six replications and in the second year after application the entire site was planted to sugar beet. Plot size was 3 m by 10 m. Field maintenance included fall moldboard plowing followed by spring field cultivation to a 10 cm depth. Prior to the second year of each study, the site was fall chisel plowing and spring culti-mulched followed by one pass with a Triple K to an 8 cm depth and cultipacked. Sugar beet plant density and visual injury were evaluated 60 days after planting. All plots were maintained weed free by a common herbicide program, cultivation and handweeding. Yield was determined by harvest of the center two rows of each plot after 1 m of border plants from each end were removed. Sugar beets were mechanically harvested and processed to determine sugar quality and recoverable white sugar per acre (8). Treatment means were computed using ANOVA and LSDs at the 5 % level of significance and data was not combined over year and location.

Campus site. A two year plant back study was initiated at the agronomy farm at Michigan State University in 1991. Nicosulfuron at 35 g/ha was applied to 25 cm corn with a tractor mounted compressed air sprayer delivering 206 L/ha of

water at 208 kPa. The year following herbicide application half the field was planted to corn and half to sugar beets. Two years after herbicide application, the field was planted entirely to sugar beets. Plot size was 3 m by 10 m and sugar beets were harvested by hand. Yields were taken from the center two rows after 1 m of border plants were removed from each end. Following herbicide application and harvest, the field was fall chisel plowed, and field cultivated twice to an 8 cm before corn and sugar beet planting. Prior to planting sugar beets in 1993, the field was disked once to a 10 cm depth, chisel plowed, and then field cultivated using a Triple "K" to an 8 cm depth. Data was subjected to ANOVA and LSD at the 5 % level of significance.

Greenhouse studies.

Growth reduction study. Characteristics of the soils used in this experiment are presented in Table 1. These soils were chosen from untreated areas of the previously described field sites. All soils except the washed sand were air dried and sieved through a 2.0 mm sieve. Large soil aggregates were either hand ground or ground by a hammer mill. Four hundred g of the non-organic soil and 200 g of organic soil were placed in 0.5 L plastic containers. Drainage holes were punched in the pots to prevent standing water from accumulating. Nicosulfuron or primisulfuron was applied using an over the top drench method and the soils were then brought to field

capacity. Application rates for both compounds were 1, 5, and 25 ppb. Each treatment was replicated three times including the untreated controls. Four Monohybrid E-4 variety sugar beets were planted in each pot in a Convicon² growth chamber for 37 days. The chamber diurnal settings were 11 hr D/ 13 hr N at 24°C with 90% relative humidity. Root and shoot fresh and dry weights were taken at harvest 37 days after planting. Two runs of the experiment were performed and combined for analysis and converted to percent of control.

Regression and correlation analyses were performed using the MSTAT³ statistical analysis program. Hyperbolic regression analysis was used to determine the IG₅₀ values. Results are presented for shoot dry weight only since all measurements showed the same trends.

Sorption/desorption study. These experiments utilized ¹⁴C labeled primisulfuron and nicosulfuron. Nicosulfuron was uniformly ring labeled on the phenyl ring and had a specific activity of 62.2 μ Ci/mg. A stock solution with a concentration of 100 ppm was made by dissolving the compound in tetrahydrofuran. Primisulfuron was uniformly labeled on the pyrimidine ring and had a specific activity of 57.9 μ Ci/mg. A 100 ppm stock solution was made by dissolving the compound in methanol. Five g of soil plus 10 ml of .01 M CaCl₂ was placed

² Convicon Corporation 3244 controller. Convicon Products of America, Pembria, ND 58271

³ Developed by the MSTAT Development Team at Michigan State University, East Lansing, MI 48824

in 25 ml glass centrifuge tubes. Soils used were the same as those used in the growth reduction study excluding the 100% sand. Five μ l of labeled stock solution was added to each tube. Various amounts of cold stock solutions were added to each tube in order to achieve total herbicide concentrations ranging from .05 ppm to 5 ppm. The range of herbicide concentration was dictated by as prior sorption isotherm trials and were below the solubility of the compounds to prevent precipitation. Sorption isotherm initial concentrations are presented on Table 2. Tubes were then capped and equilibrated on a shaker for 24 h and then centrifuged at 10,000 rpm for 10 m for the sandy loam (Campus and Freeland) and organic soils (Rose Lake) and 3,000 rpm for 5 m for the clay soils (Saginaw and Frahm). Three 1.0 ml aliquots of the supernatant were taken for liquid scintillation analysis and the rest of the liquid decanted off. These aliquots were radioassayed in a liquid scintillation spectrometer and differences between standards and supernatant were assumed to be due to soil sorption. The solution was then replaced with fresh .01 M CaCl_2 and the system was equilibrated for 24 h. Centrifuge and sampling procedures for the desorption experiment were the same as in the sorption study. Each sorption point was replicated three times.

An isotherm analysis program was developed at Michigan

State University⁴ utilizing a spreadsheet program. This program constructs Freundlich or Langmuir sorption and desorption isotherm curves on a logarithmic scale using initial and final solution concentrations of ions or radiolabeled compounds. The program also calculates R^2 values for the curves generated by the program. K_d values were calculated from sorption isotherms to express the sorptive capacity of the herbicides at equilibrium.

RESULTS AND DISCUSSION

Field Results. Visual injury ratings taken 60 days after planting the year following application were similar at the two Saginaw sites (Table 3). No injury was observed at the 70 g/ha rate of nicosulfuron and less than 10% injury was noted for 140 g/ha nicosulfuron. In contrast, sugar beets in the 40 g/ha primisulfuron plots exhibited 59 to 66% visual injury and the 80 g/ha plots a 73 to 90% reduction in above ground sugar beet growth. Primisulfuron at 80 g/ha reduced RWS⁵ from 3496 kg and 4273 kg/ha to 879 and 2175 kg/ha at the two Saginaw sites respectively. Yield, expressed as RWS, was reduced at the 40 g/ha rate of primisulfuron from 4273 to 3445 kg at one Saginaw site. No loss in yield or sugar quality occurred with any nicosulfuron treatment. By two years after application,

⁴Kathleen Remus and Boyd Ellis. Crop and Soil Sciences Dept., Michigan State University. East Lansing, MI 48824.

⁵ RWS= Recoverable White Sugar expressed in kg/ha.

there was still up to 16 % visual injury from 80 g/ha of primisulfuron but this did not affect sugar beet yield or quality.

Sugar beet response at the Freeland sites one year after application was extremely variable and, therefore, the data is not presented. No injury occurred following nicosulfuron application, however, sugar beet response in the primisulfuron treated plots was variable. Soil cores to 14 cm depth were taken adjacent to sugar beets across a range of injury levels and compared to unaffected areas within the same plots. A strong correlation was observed between sugar beet response to primisulfuron one year after application and pH (Figure 1). The marked difference in regression lines, which represent the different sites, could be attributed to dissimilarities in weather conditions between years or in site variations.

Sugar beet yield 1 year after application was not significantly reduced at the Campus site with the nicosulfuron treatment compared to the alachlor control (Table 4). In 1993, two years after nicosulfuron application, sugar beet yield was not reduced by nicosulfuron regardless of whether corn or sugar beets were planted in 1992.

Growth Reduction Results. Sugar beet response to nicosulfuron and primisulfuron for the various soils is shown in Table 5. IG_{50} (inhibit growth by 50%) values ranged from 0.8 to over 150 ppb ai for nicosulfuron and from 0.5 to 40 ppb ai for

primisulfuron. On each soil, the IG_{50} value for nicosulfuron was greater than that of primisulfuron, showing primisulfuron to be more injurious to sugar beet than nicosulfuron. Researchers at the University of Nebraska found primisulfuron to have greater soil activity than nicosulfuron using a shattercane bioassay⁶. Correlation coefficients of soil organic matter content with respect to sugar beet injury were 0.8 for nicosulfuron and 0.69 for primisulfuron (Table 6). This indicates that organic matter may be the primary binding factor in a soil system thereby reducing bioavailability. The ability of organic matter to interact with organic compounds, such as herbicides, stems from the oxygen containing functional groups found in the humic components. Soil organic matter content has been positively correlated to sulfonylurea sorption (15).

There was no correlation of sugar beet response to pH in the range of this experiment (pH 6.4 to 7.9). This data is seemingly in conflict with previous field findings that correlate soil pH to carryover potential and soil persistence (13,14,17). In this greenhouse study, herbicides were applied to the soil immediately prior to sugar beet planting. Our data indicates that although soil pH may influence the persistence of these herbicides, it does not play a major role in bioavailability.

⁶Schluefer, Personal communication. University of Nebraska. Lincoln, NE

IG₅₀ values for nicosulfuron and primisulfuron were similar for the Sand, Campus and Frahm soils but there were very large differences in the IG₅₀ values on the Saginaw, Freeland, and muck soils. There appears to be no single factor to which these differences can be attributed. Multiple regression analysis did not improve the correlation of sugar beet response to % organic matter. Since 1 ppb of primisulfuron and nicosulfuron would be equal to 0.22 g/ha in the top 15 cm of the soil profile, at least 99 % degradation and/or dilution is needed to reach the IG₅₀ concentration in the soil on some soil types. Sugar beet injury that results in yield loss, however, may still occur on field sites when herbicide concentrations are equal to 1 ppb.

Sorption studies. The sorptive and desorptive isotherms differed for nicosulfuron and primisulfuron. All non-organic soil sorption K_d values were between .299 and .866. K_d values for chlorsulfuron have been measured at 0.23-1.23 (3,4,6). Desorption K_d values for nicosulfuron are close to the sorption values although not identical. There is a larger discrepancy between sorptive and desorptive K_d values for primisulfuron. This data suggests that hysteresis occurs with both compounds but to a greater extent with primisulfuron.

Freundlich sorption and desorption isotherms were performed with the resulting R² values of .99 and also indicated a linear relationship of the data. The K_d value for primisulfuron was two to three times higher than that of

nicosulfuron (Table 5). The pK_a values of nicosulfuron and primisulfuron are 4.3 and 4.5, respectively (9, personal communication Dr. Ron Ross, Ciba). This small difference in pK_a values precludes the possibility that differences in ionization of the sulfonylurea bridge is the key factor in differential sorption.

Although primisulfuron appeared to have greater soil activity in our field and greenhouse studies compared to nicosulfuron, primisulfuron bound more tightly to soil particles, thereby becoming less available to the sugar beet. The greatest amount of sorption for both compounds occurred on the 82% organic matter soil (muck), which was reflected in the high IG_{50} values for both herbicides on the muck soil. K_d values and IG_{50} data for nicosulfuron are supportive with the exception of the Campus soil. The IG_{50} value for nicosulfuron and primisulfuron on the Campus soil would be predicted to be between 16 - 24 ppb, and 1.2 - 15.1 ppb, respectively using the equations determined by hyperbolic analysis. Findings in the Campus soil also do not support primisulfuron sorption trends. The untreated controls grew well so the possibility of site contamination with another ALS inhibiting herbicide is remote. Organic matter content and pH of the Campus soil are comparable to that of the Freeland soil so the reasons for the anomalous data from this site are still unclear.

The K_d values, and soil activity of, primisulfuron are greater than that of nicosulfuron. Therefore, increased

sensitivity of sugar beet to primisulfuron is not due to decreased sorption of primisulfuron to soil but rather the data is indicative of an inherent sensitivity of sugar beet to primisulfuron.

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TABLE 1. Characteristics of soils used in field and greenhouse studies.

SITE	%Clay	%Silt	%Sand	%OM	pH	Series
Saginaw (Site 1)	60	23	17	2.9	6.8	Mistequay silty clay
(Site 2)	58	23	19	3.1	7.4	
Frahm	52	21	27	3.8	6.4	Tappan- londo clay
Campus	26	24	49	2.9	7.6	Capac sandy loam
Freeland	28	12	59	2.8	7.9	Kawkawlin fine sandy loam
Rose Lake	-	-	-	82.0	6.4	Carlisle Muck
Sand*	0	0	100	0	6.5	-

* - Sand in this experiment was obtained from bottled washed sand treated with nutrient solution.

TABLE 2. Initial concentrations of herbicide for sorption isotherms.

Amount of 1000 ppm (unlabeled material) (ul)	Amount of 100 ppm (labeled material) (ul)	Total Herbicide (ppm)
0	5	.05
1	5	.15
2	5	.25
4.5	5	.5
9.5	5	1
24.5	5	2.5
34.5	5	3.5
49.5	5	5

Table 3. Sugar beet response to nicosulfuron and primisulfuron one and two years after application at both Saginaw Valley Research Facility sites.

		<u>Saginaw Site 1</u>					<u>Saginaw Site 2</u>				
		<u>1991*</u>		<u>1992**</u>			<u>1992*</u>		<u>1993**</u>		
<u>Herbicide</u>	<u>Rate</u>	<u>INJ Yield RWS⁷</u>	<u>g/ha</u>	<u>%</u>	<u>kg/ha</u>	<u>INJ Yield RWS</u>	<u>INJ Yield RWS</u>	<u>%</u>	<u>kg/ha</u>	<u>INJ Yield RWS</u>	<u>g/ha</u>
Nicosulfuron	35	0	40	4158	0	39	4554	0	44	5042	6
	70	0	36	3455	0	41	5310	8	42	4897	9
Primisulfuron	40	66	27	2425	2	40	4710	59	31	3445	6
	80	90	13	879	16	38	4404	73	21	2175	12
Untreated	-	0	36	3496	0	39	4565	0	37	4273	0
		4	5	544	NS	NS	NS	0	15	1781	0
LSD .05 =											

* = One year after application

** = Two years after application

⁷RWS = Recoverable White Sugar (kg/ha)

TABLE 4. Sugar beet response in 1992 and 1993 to nicosulfuron applied in 1991 at a Campus site. Ratings were combined over previous crop.

<u>Herbicide</u>	<u>Rate</u>	<u>%Injury</u>	<u>Yield</u>	<u>%Injury*</u>	<u>Yield*</u>
	(g/ha)	6/22/92	(Kg/ha)	6/23/93	(Kg/ha)
Nicosulfuron	35	15	43.5	0	52.9
Imazethapyr	71	40	42.8	5	51.5
Alachlor	2400	0	45.2	0	50.4
LSD.05=		11	NS	NS	NS

* = Combined over corn and sugar beet as previous crop from 1992.

TABLE 5. Sugar beet response to nicosulfuron and primisulfuron in greenhouse and sorption experiments.

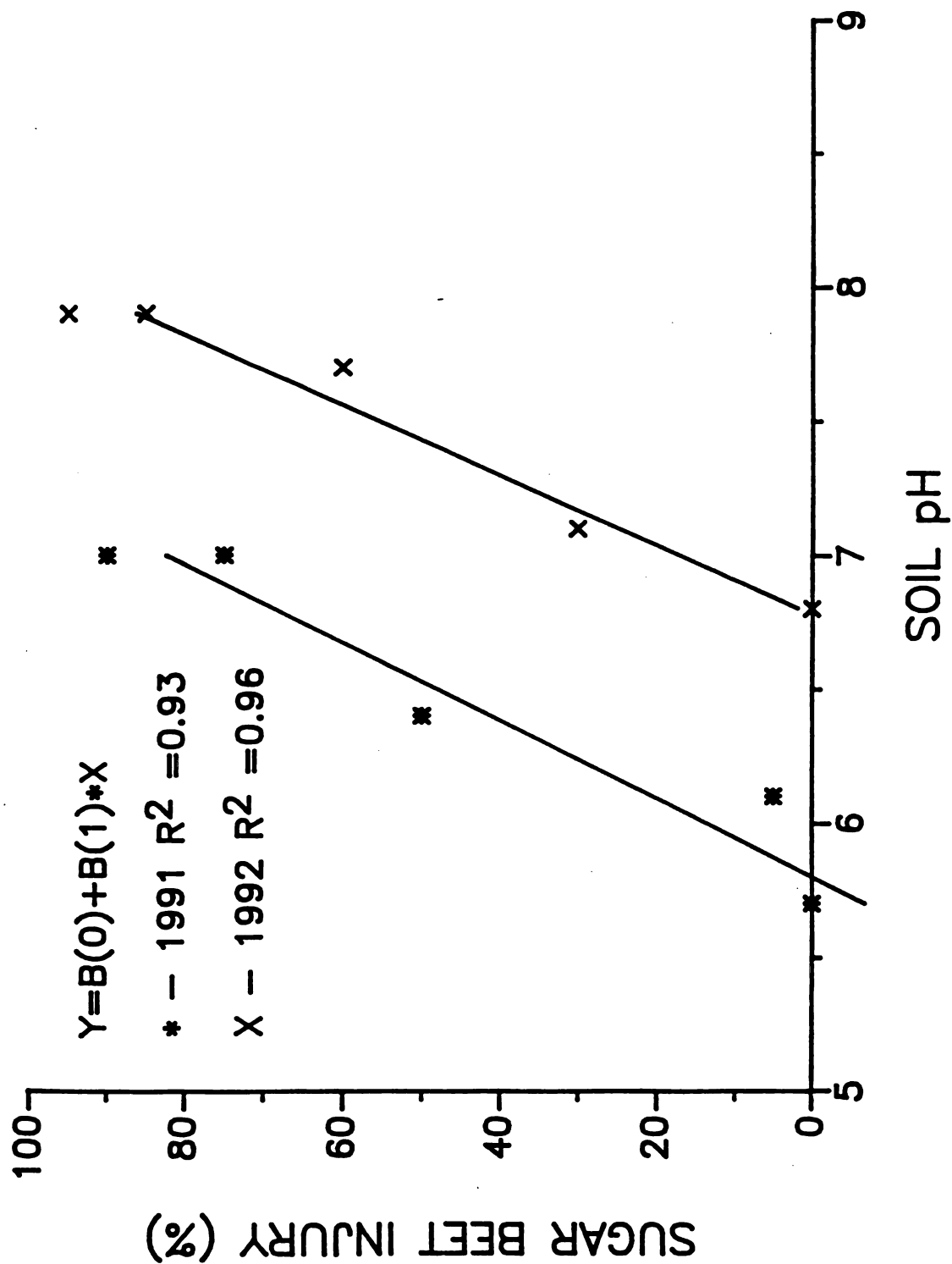
	PRIMISULFURON		NICOSULFURON	
	IG ₅₀ (ppb)	K _d	IG ₅₀ (ppb)	K _d
82 % OM	40	3.47	>150	2.58
Saginaw	2	.812	>25	.359
Frahm	15	.866	24	.523
Freeland	1	.757	16	.429
Campus	0.62	.840	1	.299
Sand	0.5	-	0.8	-

TABLE 6. Correlation Coefficients for nicosulfuron and primisulfuron at the five ppb rate analyzed over six soil types.

	Nicosulfuron R^2	Primisulfuron R^2
% Clay	-0.05	0.20
% Sand	-0.81	-0.88
% OM	0.80	0.69
pH	-0.11	-0.21

Figure 1. Sugar beet response to primisulfuron one year after application as influenced by soil pH. Each regression line represents a different site. Regression analysis on the data gave R^2 values of 0.93 and 0.96 in 1991 and 1992 respectively.

EFFECT OF SOIL pH ON SUGAR BEET INJURY FROM PRIMISULFURON ONE YEAR AFTER APPLICATION



Chapter 3

Sugar Beet Root Uptake and Translocation of Nicosulfuron and Primisulfuron.

ABSTRACT

Field studies have shown primisulfuron to be more injurious to sugar beet than nicosulfuron. Experiments were initiated to determine if primisulfuron is more injurious to sugar beet in the absence of soil and secondly to determine if the difference in sugar beet response is a result of greater uptake and translocation of primisulfuron. Hydroponic growth reduction curves were established using a modified full strength Hoagland's solution with adjusted pH values of 4.0, 5.0, 6.5 and 8.0. IG_{50} (inhibit growth by 50%) values were determined for both compounds. Primisulfuron and nicosulfuron IG_{50} values were 1.9 and 8.9 ppb, respectively, at pH 6.5. The pH of the nutrient solution did not influence sugar beet response to either herbicide. Uptake of primisulfuron was slightly greater (3%) than that of nicosulfuron (1%). Translocation (expressed as a percent of uptake) of nicosulfuron was much more rapid compared to primisulfuron. Fifty seven percent of the nicosulfuron translocated from the root by 0 hr while 48 hours were required for 60% of the primisulfuron to translocate out of the root. However, the actual amount of herbicide translocated, total ppb ai, was double for primisulfuron. The total amount of nutrient

solution taken up by sugar beet in the 12 h pulse period was 41% lower when either herbicide was present in the system compared to untreated controls. Therefore nicosulfuron and primisulfuron inhibited transpiration in sugar beet.

Nomenclature: nicosulfuron, 2-[[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]-N,N-dimethyl-3-pyridinecarboxamine; primisulfuron, 2-[[[[(4,6-bis(difluoromethoxy)-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]benzoic acid.

INTRODUCTION

Field research indicated that primisulfuron, but not nicosulfuron, persisted in soil and injured sugar beets planted one year after application (6). The difference in response of sugar beet to nicosulfuron and primisulfuron, two sulfonylurea herbicides, may be due to differences in soil persistence or to differences in sugar beet tolerance to these two herbicides.

Soil pH influences crop response to sulfonylureas. Persistence increases due to a decrease in chemical hydrolysis as soil pH is increased (8,9). Sugar beet response to primisulfuron has been observed in the field to be directly related to pH (6).

Tolerance of johnsongrass (Sorghum halapense L.), Eastern black nightshade (Solanum ptycantum L.), barnyardgrass (Echinochloa crus-galli Beav.), and giant foxtail (Setaria

faberi Herrm.) to nicosulfuron and primisulfuron varies by species and herbicide (5). Both metabolism and variations in ALS site sensitivity have been implicated in the differences in response of these species to nicosulfuron and primisulfuron.

Hydroponic experiments were conducted to determine if solution pH influenced sugar beet response to primisulfuron and nicosulfuron and if differences occurred in sugar beet response to these two herbicides in the absence of soil. Uptake and translocation of nicosulfuron and primisulfuron in sugar beet were measured to determine if increased sugar beet sensitivity was related to greater uptake and/or translocation.

MATERIALS AND METHODS

IG₅₀ studies at various pH. Mono-hybrid E-4 variety sugar beets were germinated for 7-10 days in a washed sand medium spiked with 250 ml of a modified Hoagland's solution (2). When seedlings reached cotyledon to first leaf pair, plants were transferred to 125 ml glass jars wrapped in aluminum foil containing 120 ml of full strength modified Hoagland's solution. Jars were placed in a growth chamber with diurnal settings of 11 hr day/ 13 hr night at 24°C with 90% relative humidity. Nutrient solution pH was either 4.0, 5.0, 6.0, 6.5 or 8.0. Since this was a non-aerated system, nutrient solution

was changed every two to three days. Seedlings were supported by glass wool. After a 10 day acclimation period in an untreated system, sugar beet roots were exposed to 5 or 25 ppb ai of either nicosulfuron or primisulfuron. Plants at pH 6.5 were also exposed to 1 ppb ai. Fourteen days after treatment plants were harvested. Root and shoot fresh and dry weights were measured and hyperbolic regression analysis performed on the root dry weight data only since trends were similar for all measurements. The MSTAT^a statistical program was used for correlation and separation of treatment means at the 5 % significance level using Fisher's protected LSD. The experiment consisted of 4 replications of each concentration of nicosulfuron and primisulfuron plus four control vials containing no herbicide. Two runs of the experiment were performed and data was combined for analysis.

Uptake and translocation study. The experimental procedure was the same as the IG₅₀ experiment with the following exceptions:

Plants were transferred to vials containing 100 ml of nutrient solution with a pH of 6.8. Twenty-one days after transfer, plant roots were exposed to 5 or 25 ppb ai of ¹⁴C-labeled nicosulfuron or primisulfuron for 12 h (7). Nicosulfuron was uniformly ring labeled on the phenyl ring and had a specific activity of 62.2 μ Ci/mg. Primisulfuron was uniformly labeled on the pyrimidine ring and had a specific

^aProgram developed by the MSTAT Development Team at Michigan State University East Lansing, MI 48824

activity of 57.9 $\mu\text{Ci}/\text{mg}$. After the 12 h pulse period, plant roots were rinsed and transferred to vials containing 100 ml of untreated solution. Four sugar beets at each time interval were harvested. Sample times were 0, 4, 8, 12, 24, 48, and 144 h after pulsing. Root and shoot fresh weights were taken at harvest and plant parts were combusted in a biological oxidizer. Data were combined over experiment and ANOVA and LSD at the 5 % significance level were performed. Regression and correlation analysis were also executed on the untransformed data. Radioactivity in the system was quantified using liquid scintillation.

RESULTS AND DISCUSSION

Hydroponic Studies. Primisulfuron concentrations of 1, 5 and 25 ppb reduced sugar beet root and shoot dry weight more than comparable concentrations of nicosulfuron (Table 1). Varying the pH of the nutrient solution did not influence sugar beet response (Table 2). The predominant species of both nicosulfuron and primisulfuron at pH 4.0 would be the neutral species while at pH 8.0 both compounds would be mostly ionized. Ion or acid trapping mechanisms have been suggested to be the method through which sulfonylureas enter the root of plants (4). If this were the sole method of entry, then more herbicide should enter the plant at a lower pH. The data indicates that another method of entry, such as passive uptake, occurs in conjunction with the ion trapping mechanism. Increased sugar beet injury has been noted at high soil pH

(6,8,9) when the molecule would predominantly exist in negative state (1,3) and in the absence of soil pH did not affect sugar beet response. This shows the effect of pH to be related to the persistence of nicosulfuron and primisulfuron.

Hyperbolic regression analysis was performed on the data and equations for each line determined (Figure 1). Estimated IG_{50} (inhibit growth by 50%) values for nicosulfuron and primisulfuron are 8.9 and 1.9 ppb ai, respectively. This data indicates that differential tolerance in sugar beet may play a significant role in greater sugar beet response to primisulfuron in the field.

Uptake and translocation. Only 1 % of the total amount of nicosulfuron was taken up by sugar beet roots, while roots exposed to primisulfuron took up 3 % of the herbicide at the 25 ppb rate. Sugar beet uptake at a concentration of 5ppb was .9% for nicosulfuron and 2.5% for primisulfuron. Sugar beets exposed to a 25 ppb concentration of primisulfuron were visibly injured within 48 hours of pulsing. Injury symptoms also appeared with primisulfuron concentrations of 5 ppb but the injury did not become apparent until six days after treatment. Nicosulfuron treated plants showed slight injury six days after pulsing at 25 ppb, but the extent of the injury was not as severe as that of primisulfuron. The slight difference in uptake between these compounds did not account for the observed differences in sugar beet response when subjected to ANOVA.

The translocation patterns of these two herbicides were dissimilar (Figure 2). Although there was no significant difference in the total amount of herbicide translocated (expressed as a percent of uptake) after 144 hours, nicosulfuron translocated 57 % out of the treated root at the 0 hour sampling time. A similar amount of primisulfuron was not translocated until 48 hours after pulsing. The actual total amount of nicosulfuron that moved to the site of action was .20 ppb ai. Sugar beet translocated a total of .43 ppb ai of primisulfuron in the same time interval. Statistical analysis determined that there was no significant correlation of sugar beet response to uptake and/or translocation.

Transpiration rates of sugar beet, as calculated by the amount of nutrient solution taken up during the pulse period, were similar for both compounds. Nutrient solution taken up by sugar beet was 41 % less (3.4 ml and 3.5 ml) than that of the untreated control (8.6 ml) in the presence of herbicide. This indicates that both nicosulfuron and primisulfuron inhibited transpiration which may account for the lack of uptake of either herbicide, regardless of concentration. Nicosulfuron should have reduced transpiration more quickly than primisulfuron since translocation was much more rapid. Since this was not the case, another mechanism must confer tolerance of nicosulfuron to sugar beet, such as more rapid metabolism and/or reduced ALS sensitivity compared to primisulfuron.

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Table 1. Sugar beet response to nicosulfuron and primisulfuron in hydroponics at pH 6.5.

Herbicide	Rate (ppb)	Root dry weight (% of Control)	Shoot dry weight (% of Control)
Nicosulfuron	1	75	95
	5	62	88
	25	40	52
Primisulfuron	1	66	75
	5	29	38
	25	15	25

LSD (.05) = 27

22

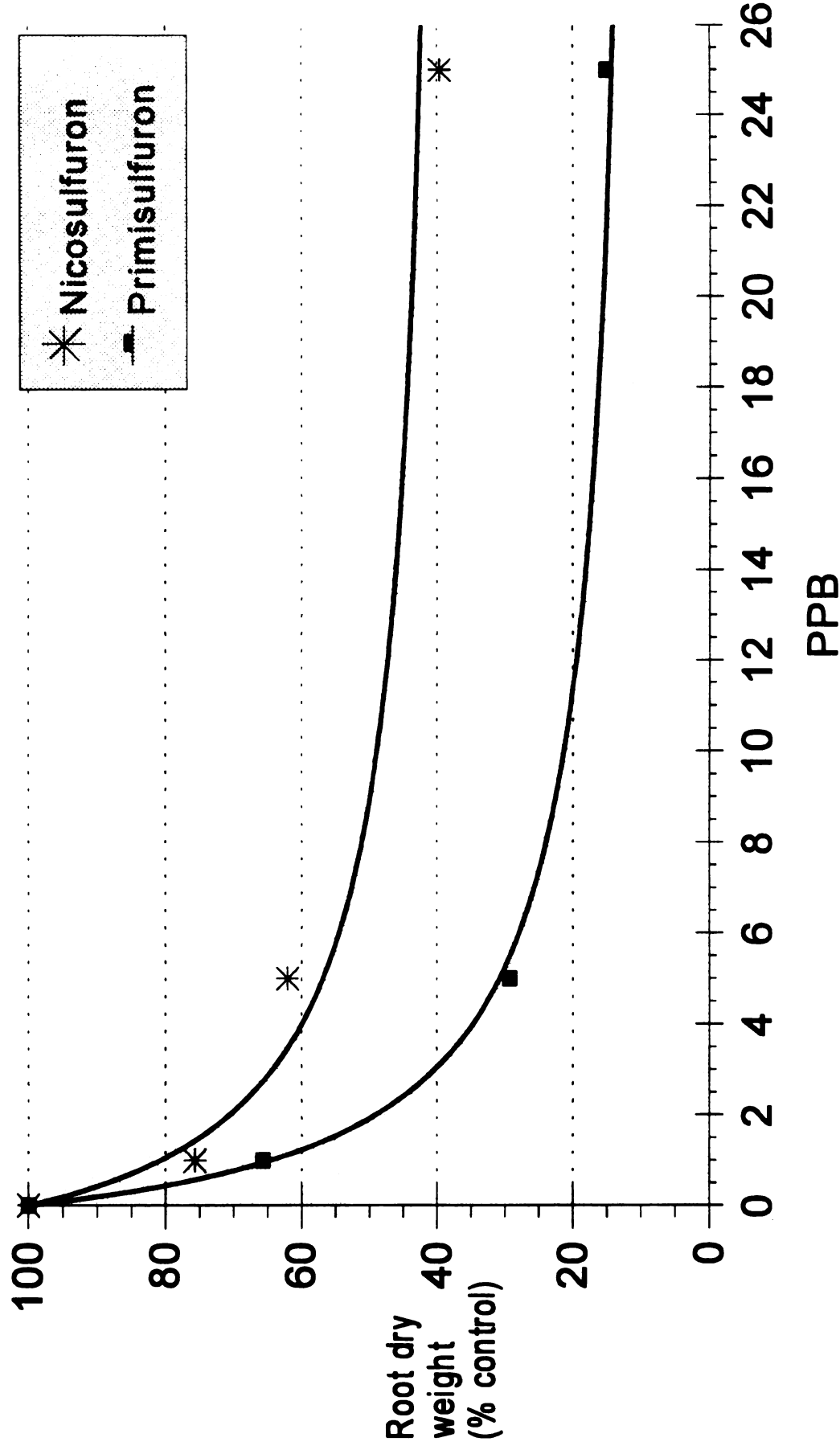
Table 2. Sugar beet response to nicosulfuron and primisulfuron at various pH values.

Herbicide	Rate ppb	pH 4.0 Shoot dry weight as a % of control	pH 5.0 Shoot dry weight as a % of control	pH 6.0 Shoot dry weight as a % of control	pH 8.0 Shoot dry weight as a % of control
Nicosulfuron	5	98	100	95	100
	25	91	77	100	88
Primisulfuron	5	79	75	88	71
	25	40	50	55	53

LSD .05 = 22 20 18 21

Figure 1. Hyperbolic regression curves showing sugar beet response to nicosulfuron and primisulfuron at pH 6.5. Analysis was performed on root dry weight data since trends for all measurements were similar.

Hydroponic Sugar beet Response

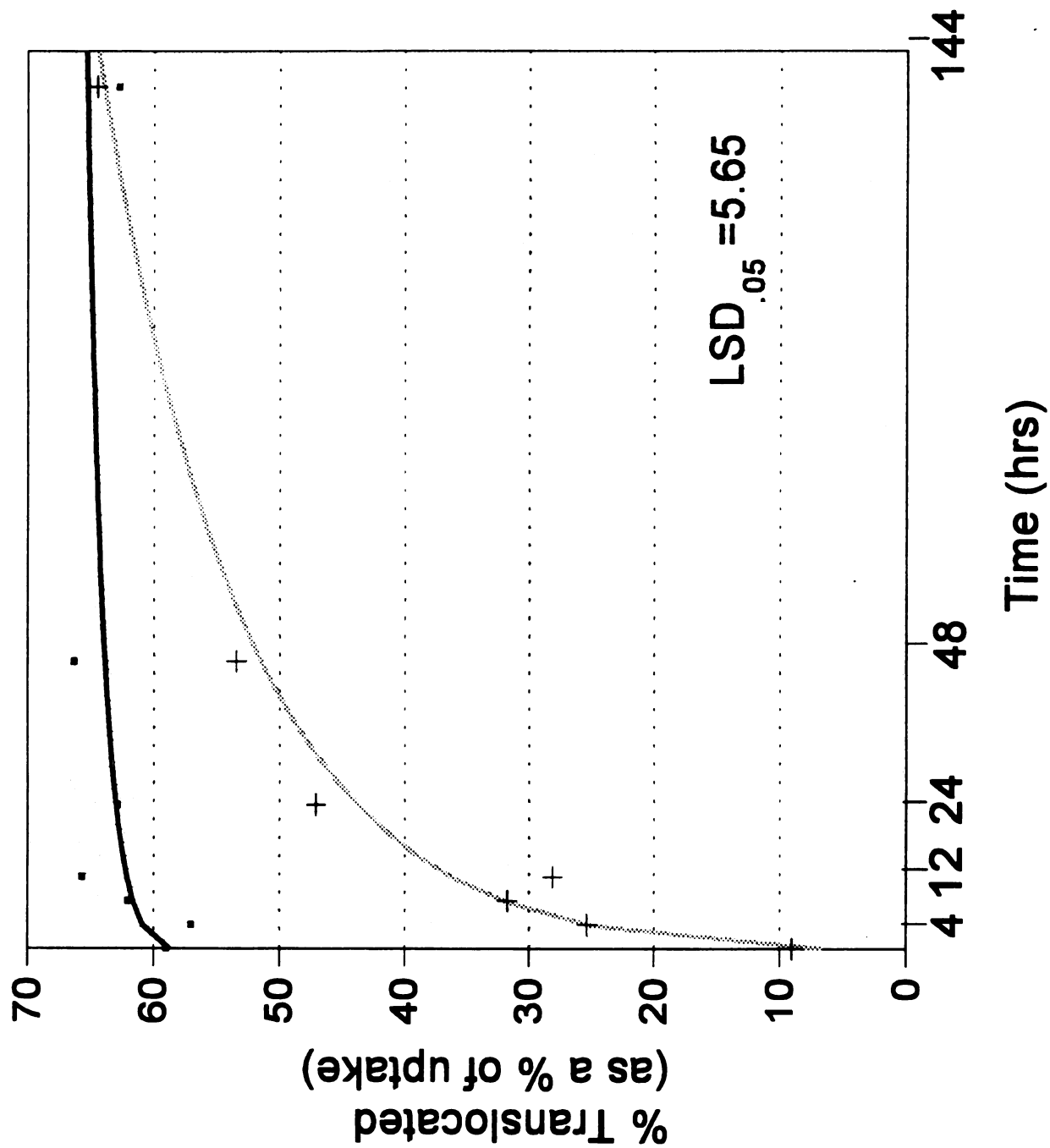


$$\text{Nicosulfuron } \% \text{Control} = 100 - (27.6 * \text{ppb}) / (1 + (27.6 / 62.7) * \text{ppb}) \quad R^2 = .567$$

$$\text{Primisulfuron } \% \text{Control} = 100 - (57.5 * \text{ppb}) / (1 + (57.5 / 91.1) * \text{ppb}) \quad R^2 = .850$$

Figure 2. Translocation of ^{14}C -labeled nicosulfuron and primisulfuron in sugar beet at pH 6.8. Translocation is presented as a percent of control.

Translocation vs Time



• Nicosulfuron
+ Primisulfuron

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